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A STUDY OF MANGANESE PHOSPHATING REACTIONS



TECHNICAL REPORT

Joseph Menke

September 1971

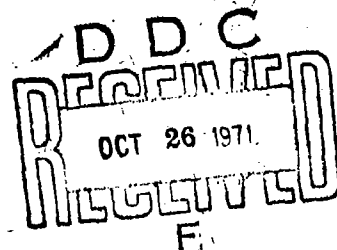
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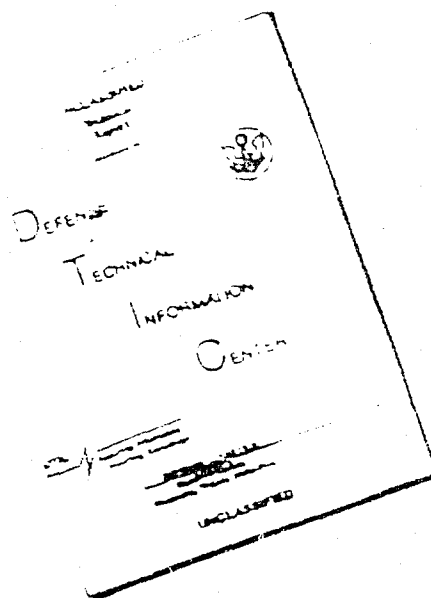
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ABSTRACT

Work was conducted by the Research Directorate, Weapons Laboratory at Rock Island, Research, Development and Engineering Directorate, U. S. Army Weapons Command to determine the composition of and the reactions associated with the formation of manganese-phosphate coatings. An improved phosphate coating was studied as produced from a stock manganese phosphating bath to which an addition of manganese citrate, tartrate, or gluconate was made. Processing was accomplished in an autoclave at temperatures above 212°F with steam pressure. The coatings produced by conventional and pressure methods were examined by differential thermal analysis, X-ray diffraction, and atomic absorption analysis. The chemical structure of the conventional coating was $\text{Fe}_3(\text{PO}_4)_2 \cdot 2\text{MnHPO}_4 \cdot 4\text{H}_2\text{O}$, a form of hureaulite, and that of the pressure phosphate coating was mainly manganese phosphate heptahydrate, $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$.

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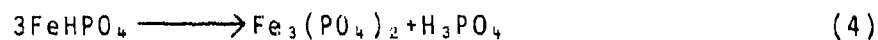
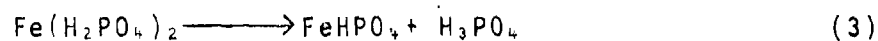
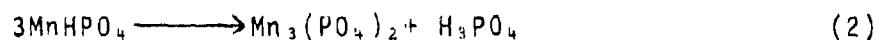
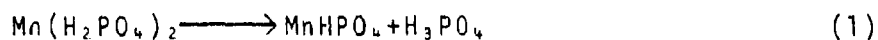
OBJECTIVE

The objective of this project was to study the reactions which occur when metal-organic compounds are added to conventional manganese-phosphating solutions during application of pressure phosphate-coatings.

BACKGROUND

Manganese-phosphate coatings have been applied to ferrous materials for many years. The coating consists of an insoluble metal phosphate which is formed in a solution of phosphoric acid and other chemicals. Corrosion resistance obtained with a bare manganese-phosphate coating is usually limited, (about two hours in 5 per cent salt spray). Therefore, the coating usually serves as a base for various supplementary finishes. When supplementary coatings such as oils or paints are applied over phosphate coatings, the corrosion resistance is increased; however, improvement of the inherent value of the phosphate coating itself is highly desirable. Recent research is involved with the development of a manganese-phosphate coating that provides a significant increase in salt-spray corrosion resistance (i.e., in excess of 500 hours) when compared with conventional manganese-phosphate coatings. This improved manganese-phosphate coating also has excellent corrosion resistance after being heated for an hour at temperatures of 450°F. With conventional manganese-phosphate coatings, heated to 450°F, salt-spray corrosion resistance is severely reduced.

The reactions involved in the formation of a conventional manganese-phosphate coating are complex. The process may best be described as a combination of the following reactions:



Manganese dihydrogen phosphate, $\text{Mn}(\text{H}_2\text{PO}_4)_2$, is soluble in the water-phosphoric acid solution. When a steel specimen is immersed into the acidic solution, iron is dissolved and

hydrogen gas is evolved. As the pH at the solution-specimen interface increases because of hydrogen ion depletion, the gassing ceases and insoluble manganese hydrogen phosphate, MnHPO_4 , is formed, (1). Dissolved iron from the specimen and iron in solution can also form an insoluble iron hydrogen phosphate, FeHPO_4 , which may become a part of the coating, (3). A further increase in the interface pH results in the formation of manganese phosphate, $\text{Mn}_3(\text{PO}_4)_2$ or iron phosphate, $\text{Fe}_3(\text{PO}_4)_2$. (See equations (2) and (4).) Thus, dependent upon the solution equilibrium, manganese hydrogen phosphate, iron hydrogen phosphate, manganese phosphate, and iron phosphate can all be present in the final coating. The possible presence of various compounds in the manganese-phosphate coating is also indicated by X-ray analysis. According to the analysis, the coating has the following structure: $(\text{Fe,Mn})_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$. This is the structure of hureaulite, a naturally occurring phosphate mineral. The structure of hureaulite can be represented in the following arrangements: $\text{Fe}_3(\text{PO}_4)_2 \cdot 2\text{MnHPO}_4 \cdot 4\text{H}_2\text{O}$ or $\text{Mn}_3(\text{PO}_4)_2 \cdot 2\text{FeHPO}_4 \cdot 4\text{H}_2\text{O}$.

The reactions involved in the formation of the improved manganese-phosphate coating are much more complex. The coating is formed in an autoclave at temperatures above 212°F with the use of a conventional manganese-phosphating solution to which is added a metal-organic compound. This project was undertaken to determine the mechanism or reactions involved in the formation of the improved phosphate coating and to determine the causes involved in the improvement of corrosion protection.

APPROACH

Work concurrently being conducted and unreported at the time of this writing has led to process variations of steam pressure and metal-organic chemical additions that produce manganese-phosphate coatings of exceptional corrosion resistance. Coatings were produced under some of these process conditions for study and analysis in this work.

Specimens of SAE 1020 steel, 2"x3"x1/16", 1"x1"x1/16" and 2"x6"x1/8" were vapor-degreased and abrasive-blasted with steel grit. One group of the specimens was processed in a conventional manganese-phosphating bath to which 10 grams per liter of manganese citrate had been added. Processing was accomplished in an autoclave at 22 psig (260°F) of steam pressure for 15 minutes. A second group of the specimens was processed in a conventional manganese-phosphating bath

to which 10 grams per liter of manganese tartrate had been added. Processing was accomplished in an autoclave at <1 psig (214°F) of steam pressure for 30 minutes. A third group of the specimens was processed in a conventional manganese-phosphating bath to which 10 grams per liter of manganese gluconate had been added. Processing was accomplished in an autoclave at <1 psig (213°F) of steam pressure for 30 minutes.

To determine how the higher temperature attained at 22 psig would affect the phosphating solution when steel specimens were not being processed, solutions were heated in an autoclave at 22 psig (260°F) of steam pressure for 15 minutes. One solution contained 10 grams of manganese citrate per liter added to a conventional manganese-phosphating bath; the other solution was a conventional manganese-phosphating bath with no additives.

Specimens were also coated with conventional manganese-phosphate so that atomic absorption, differential thermal analysis, and X-ray diffraction data could be correlated with the pressure coating data. Sludge, which formed during some of the processing or heating cycles, was filtered out, dried at 212°F, and subjected to various analytical procedures. Analyses of solutions are given in Table I, and analyses of coatings and sludge are in Table II. Some of the pressure manganese-phosphated specimens (2"x3"x1/16") were heated in a muffle furnace at 400°F, 800°F, 1000°F, and 1200°F for one hour and were then subjected to the 5 per cent salt-spray test. The remaining pressure phosphate-coated specimens, not heated, were tested as-processed. Specimens (1"x1"x1/16") coated with conventional and pressure manganese-phosphate were subjected to X-ray diffraction analysis. A known, reagent grade manganese-phosphate powder was also subjected to X-ray diffraction analysis as a standard. Conventional and pressure manganese-phosphated specimens (2"x6"x1/8") were scraped to obtain samples of the coating for differential thermal analysis and for atomic absorption analysis.

An intensive literature search was conducted for chemical reactions that could be associated with the formation of phosphate coatings under the influence of steam pressure and metal-organic additives.

TABLE I

ANALYSIS OF SOLUTIONS USED TO EVALUATE PRESSURE MANGANESE-PHOSPHATE COATINGS

Solution	Free Acid Points (FA)*	Total Acid Points (TA)*	Ratio (TA/FA)	% Iron
Stock Mn-phosphating bath	3.8	38.7	10.1	0.06
Stock bath w/ 10 g/l Mn citrate	2.5	37.3	14.9	0.05
Bath after processing at 22 psig	8.0	37.6	4.7	0.04
Stock Mn-phosphating bath	4.6	39.0	8.5	0.05
Stock bath w/ 10 g/l Mn tartrate	3.6	40.7	11.3	0.04
Bath after processing at 214°F	8.4	39.2	4.6	0.05
Stock Mn-phosphating bath	4.2	38.3	9.1	0.05
Stock bath w/ 10 g/l Mn gluconate	2.9	40.0	13.8	0.05
Bath after processing at 213°F	7.6	37.3	4.9	0.04
Stock Mn-phosphating bath	4.6	31.0	1.9	0.04
Stock bath w/ 10 g/l Mn citrate	1.5	28.8	9.2	0.03
Bath after application of 22 psig**	4.8	28.6	6.0	0.03
Stock Mn-phosphating bath	3.0	31.0	10.3	0.03
Bath after application of 22 psig**	5.7	29.8	5.2	0.03
Conventional Mn-phosphating bath	2.9	25.5	8.8	0.21

*Titrating with 0.1 N NaOH, a point is equivalent to one milliliter of 0.1 N NaOH.

**No specimens were processed.

TABLE II

ATOMIC ABSORPTION ANALYSIS OF VARIOUS
PHOSPHATE MATERIALS FOR IRON AND MANGANESE

Material Analyzed	% Iron	% Manganese
Conventional manganese-phosphate coating	26.6	12.5*
Pressure manganese-gluconate coating	2.0	30.0
Sludge formed during pressure gluconate processing	2.8	26.0
Pressure manganese-citrate coating	2.6	28.0
Sludge formed during pressure citrate processing	2.0	26.0
Pressure manganese-tartrate coating	2.0	31.0
Sludge from a stock manganese solution heated to 260°F without specimens	3.2	22.5**
Reagent Grade $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$	0.0	33.0
Commercially available $\text{Mn}(\text{H}_2\text{PO}_4)_2$	0.2	16.2***

*Black residue in the test solution.

**Test solution a little cloudy.

***White residue in the test solution.

RESULTS

Pressure manganese-phosphate coatings heated in a muffle furnace at 400°F for one hour did not change in physical appearance. Heating at 800°F for one hour caused the coating to turn green after going through a transitional brown color at atmospheres between 500°F and 700°F. The heating of pressure manganese-phosphate coating at 1000°F resulted in a green finish. After the coating was heated at this temperature, tiny areas of it spalled when the specimens were removed from the furnace; this was probably caused by thermal shock during cooling. The relative amount of spalling that was observed could be summarized as follows:

citrate >> tartrate > gluconate

Immediately after the specimens were removed from the furnace after heating to 1200°F for one hour, all the pressure coatings were intact. Within five minutes, more than 90 per cent of all the coatings had spalled. The corrosion resistance of heated and unheated coatings is summarized in Table III.

Examination of the coatings spalled at 1200°F showed that the pressure manganese-phosphate finish consisted of two layers. The layer closest to the basis metal was gray, and was relatively smooth and crystalline, much like a conventional manganese-phosphate coating. The outer coating was green with a coarse crystalline structure. The spalled coating segments were returned to the furnace at 1200°F for one hour to determine whether all the coating would become green if the initial conversion to the green color was just a surface phenomenon. Examination of the coating after this second heating showed that the two distinct layers were still present. The pressure manganese-citrate bath coating also had small areas that were yellow. These yellow areas, like the green coating, were not present in the basic gray coating.

Differential thermal analysis of coating material scraped from the specimen surface showed that conventional manganese-phosphate coatings undergo some type of exothermic deterioration before an endothermic reaction. Interpretation of the differential thermal analysis data is difficult because the reactions associated with the various differential thermal peaks are unavailable at the present time.

A previous examination of X-ray diffraction data by Crain¹ indicated that the conventional and pressure manganese-phosphate coatings were essentially alike. However, two diffraction peaks in the pressure manganese-citrate X-ray

TABLE III

CORROSION RESISTANCE OF HEATED AND UNHEATED
PRESSURE MANGANESE PHOSPHATE COATINGS

Processing Additive	Thermal Treatment	Hours of 5 per cent Salt-Spray Exposure				
		1	24	100	120	1500
Mn citrate	None	OK	OK	OK	OK	OK
Mn tartrate		OK	OK	OK	OK	OK
Mn gluconate		OK	OK	OK	OK	OK
Mn citrate	1 hour @ 400°F	OK	OK	OK	OK	OK
Mn tartrate		OK	OK	OK	OK	OK
Mn gluconate		OK	OK	OK	OK	OK
Mn citrate*	1 hour @ 800°F	OK	Failed	Failed	-	-
Mn tartrate*		OK	OK	Failed	-	-
Mn gluconate*		OK	OK	OK	Failed	-
Mn citrate**	1 hour @ 1000°F	Failed	-	-	-	-
Mn tartrate**		Failed	-	-	-	-
Mn gluconate**		Failed	-	-	-	-

*Removed from test after 150 hours' exposure.

**Removed from test after 24 hours' exposure.

diffraction pattern are more intense when compared with the diffraction pattern for conventional manganese-phosphate. These two peaks correspond to the two major peaks present in the X-ray diffraction pattern of manganese pyrophosphate. To date, the presence of pyrophosphate in the pressure phosphate-coating has not been confirmed.

X-ray diffraction analysis conducted during this investigation showed that the diffraction pattern of conventional manganese-phosphate is similar to the diffraction pattern of hureaulite. The X-ray diffraction pattern of pressure manganese-phosphate coatings more closely resemble the diffraction pattern of manganese-phosphate heptahydrate, $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$. Some peaks in the diffraction pattern of the pressure phosphate-coatings are more intense than those in the diffraction pattern of $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$. These peaks, two major and four minor, correspond to the six most intense peaks of manganese pyrophosphate. The intensity increase due to the possible presence of manganese pyrophosphate is the most pronounced in the pressure manganese-citrate coating.

Atomic absorption analysis included a determination of the manganese and iron content of various phosphate coatings, processing sludges, and other iron-manganese compounds. The results of the atomic absorption analyses are shown in Table II. The iron content of the conventional manganese-phosphate coating was 26.6 per cent and the manganese content was 12.5 per cent. These percentages correspond with the respective iron and manganese content of $\text{Fe}_3(\text{PO}_4)_2 \cdot 2\text{MnHPO}_4 \cdot 4\text{H}_2\text{O}$. Since the pH at which iron phosphate begins to form is lower than the pH at which manganese phosphate begins to form,² the formation of iron phosphate would predominate and be present in greater concentration. Composition of the conventional manganese-phosphate coating is thus influenced largely by the initial pH at which the coating begins to form.

Atomic absorption analysis of pressure manganese-phosphate coatings shows that the major constituent is manganese with a small amount of iron being present. Since manganese ion is present to a much greater extent than iron in the processing solution, the composition of a pressure manganese-phosphate coating is influenced by the precipitation of manganese-phosphate because of inverse solubility. Most compounds become more soluble when the solution temperature increases. Compounds which become less soluble with increasing temperature exhibit inverse solubility. Manganese, zinc, and iron phosphates are all inversely soluble, and precipitation increases as the temperature rises.

DISCUSSION

The reactions associated with the formation of a pressure manganese-phosphate coating must take into consideration two major factors: (1) the addition of manganese citrate, tartrate, or gluconate and (2) the inclusion of processing parameters above 212°F by steam pressure. The reactions which may occur when manganese citrate, tartrate, or gluconate are added to a phosphating solution can be summarized by consideration of the fact that organic radicals can:

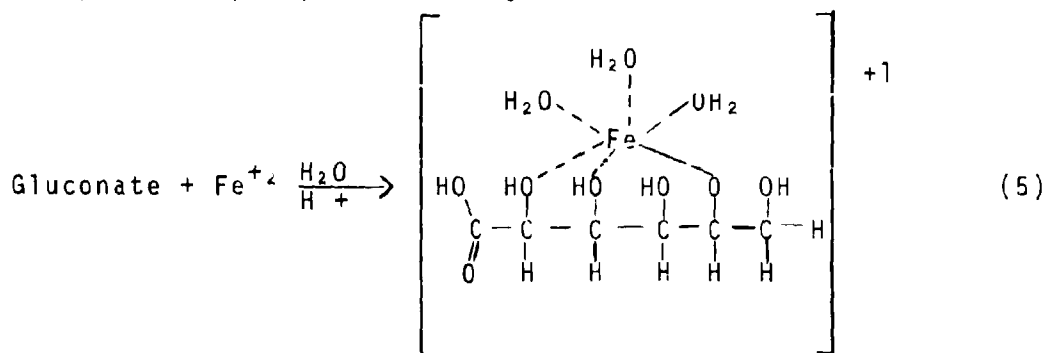
1. Serve as metal ion sequestrants.
2. Buffer the solution, i.e., change free acid and pH.
3. Affect the specimen interface pH, i.e., lower the pH at which the coating forms.
4. Affect the solubility of the metal hydrogen-phosphate formed.
5. Serve as a cathodic depolarizer.
6. Increase the available manganese-ion content of the phosphating solution.

When the phosphating solution is heated above 212°F under steam pressure during processing, the reactions may:

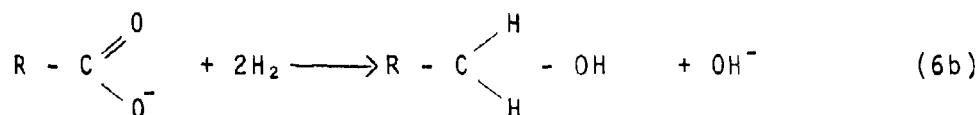
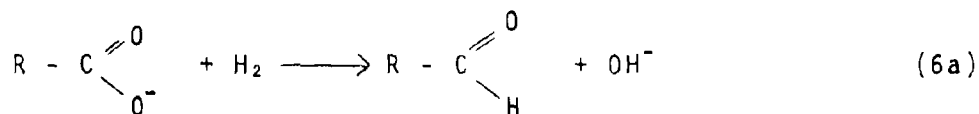
1. Promote inverse solubility formation of metal phosphates.
2. Affect the possible formation of pyrophosphate and water from orthophosphate.
3. Increase the solubility of manganese citrate, tartrate, and gluconate.
4. Increase the free acid as a result of the formation of the phosphate coating and precipitation of iron-manganese phosphate sludge.

Of the above-mentioned reactions, the following equations are considered of greatest importance in the formation of

the pressure phosphate coating:

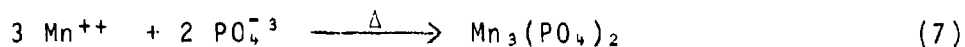


The organic radicals, citrate, tartrate, and gluconate, can serve as iron sequestrants and buffers. Their presence in a phosphating bath would reduce the iron present in the initial pressure phosphate layer and would increase the specimen-solution interface pH; thus manganese-phosphate coating is formed more quickly.

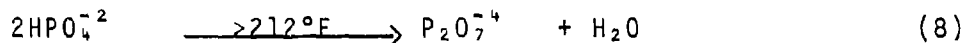


The organic radical could be used as a cathodic polarizer, thus the formation of the phosphate coating would be speeded up by reaction with gaseous hydrogen liberated during pickling. Reaction with hydrogen may render the organic radical optically inactive and account for its apparent concentration decrease in the phosphating solution. Since no optically active organic constituent is present in the sludge and no apparent reason is advanced for any organic radicals in the phosphate coating, the only place in which the organic constituent can remain is in solution. Analysis of the processing solution

with the use of optical rotation techniques, reveals that the organic constituent is decreased from 1.0 to approximately 0.5 per cent.



The manganese-ion content is increased by the addition of manganese citrate, tartrate, or gluconate to the phosphating solution. This increase and the inverse solubility characteristic of manganese phosphate (as the temperature rises) drives the reaction (7) to the right; this action indicates that the greater portion of the pressure coating should be manganese phosphate. This condition results in a coating that contains very little iron phosphate. Atomic absorption analysis and X-ray diffraction data support the conclusion that the major constituent in the pressure coating is manganese phosphate.



Processing in a phosphating bath above 212°F with steam pressure could result in the formation of manganese pyrophosphate in addition to the manganese phosphate formed by inverse solubility (8). X-ray diffraction data indicate that the presence of manganese pyrophosphate is possible. Phosphating solution at higher temperatures provide greater possibility of the formation of pyrophosphate.

CONCLUSIONS

1. The formation of a conventional manganese-phosphate coating is dependent on pH changes which occur at the specimen-solution interface.
2. The composition of a conventional manganese-phosphate coating is $\text{Fe}_3(\text{PO}_4)_2 \cdot 2\text{MnHPO}_4 \cdot 4\text{H}_2\text{O}$.
3. The formation of the pressure phosphate-coating is largely dependent on the inverse solubility precipitation of manganese phosphate.
4. The pressure manganese-phosphate coating consists of two distinct layers, a basis manganese-phosphate coating covered by a coating of manganese phosphate containing a limited amount of manganese pyrophosphate.

5. The chemical reactions in phosphating solutions modified as indicated in this work are capable of producing coatings with exceptional resistance to heat and corrosion.

RECOMMENDATIONS

Further work should be conducted to determine:

1. the inverse solubility of manganese phosphate at various temperatures;
2. the pH at which the phosphate coating begins to form in conventional manganese-phosphating solutions and in solutions to which manganese citrate, tartrate, and gluconate have been added;
3. the effects of increasing temperature on the pH at which conventional and pressure phosphate-coatings form;
4. the effects of iron on the corrosion resistance of conventional phosphate coatings.

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